REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-04-

0532

1. REPORT DATE *(DD-MM-YYYY)* 28-09-04	**2. REPORT TYPE** DURIP-final	**3. DATES COVERED** *(From - To)* 05/01/03 - 04/30/04
4. TITLE AND SUBTITLE Instrumentation for the Rapid Discovery and Mechanistic Understanding of Non-Chromate Inhibitors		**5a. CONTRACT NUMBER** N/A **5b. GRANT NUMBER** F49620-03-1-0315 **5c. PROGRAM ELEMENT NUMBER** N/A
6. AUTHOR(S) S. R. Taylor		**5d. PROJECT NUMBER** N/A **5e. TASK NUMBER** N/A **5f. WORK UNIT NUMBER** N/A
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Virginia Office of Sponsored Programs P.O. Box 400195 Charlottesville, Virginia 22904		**8. PERFORMING ORGANIZATION REPORT NUMBER** UVA 118852-101-GG10531-31340
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research 4015 Wilson Blvd, Rm. 713 Arlington, Virginia 22203 NL		**10. SPONSOR/MONITOR'S ACRONYM(S)** N/A **11. SPONSOR/MONITOR'S REPORT NUMBER(S)** N/A

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release, distribution unlimited.

20041028 077

13. SUPPLEMENTARY NOTES

14. ABSTRACT

A significant obstacle to the identification of alternate corrosion inhibitors is the slow pace of screening candidate compounds. The test matrix that accounts for operational variables is expansive, especially when the question of synergy is included. This research has acquired instrumentation that will significantly improve experimental throughput for inhibitor screening, as well as provide a means to understand the mechanism of single and multiple inhibitor behavior. This research program has purchased a plate reader, a Multi-Micro-electrode Array, an electrochemical quartz crystal microbalance, and a Raman spectrometer. To date, these instruments have increased experimental throughput by a factor of 100+. These instruments will also provide meaningful student training in the understanding of structure-performance relationships of corrosion inhibitors needed by the Department of Defense.

15. SUBJECT TERMS

Non-chromate corrosion inhibitors, high throughput screening, inhibitor synergy

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Taylor, S. R.
a. REPORT Unclassified	**b. ABSTRACT** Unclassified	**c. THIS PAGE** Unclassified	UL	4	**19b. TELEPHONE NUMBER** *(include area code)* 601-984-6170

I. Introduction

A Multi-Disciplinary University Research Initiative (grant number F49602-01-1-0352) was initiated in May 2001 to develop the scientific basis for a multi-functional aerospace coating using nano-engineering methods. Central to this MURI is the identification of an environmentally benign compound to replace chromate-based inhibitive pigments used in present day aerospace primers. Management of chromate-based materials represents a significant fraction of the $1 to $3 billion structural maintenance costs spent by the Air Force each year[‡].

Numerous compounds have been examined through the years with the hope of providing a chromate replacement. These compounds include molybdates[1], vanadium-based compounds[2], boron-based compounds[3-5], and rare earth salts[6], among others. Many of these compounds have been examined recently for inhibitor efficacy on aerospace alloys[6-8]. However, to date, no single compound has demonstrated a corrosion inhibition power (efficiency at specified concentration) comparable to chromate.

A promising alternative to the use of a single inhibitor species is that of using synergistic combinations of two or more compounds. Synergy occurs when the inhibitive property of the combination exceeds the arithmetic sum of the individual components. Synergistic combinations of inhibitors have been examined extensively for steel in acidified[9-16] and neutral[17-20] aqueous environments, as well as for copper in neutral aqueous environments[21-22]. Numerous theories for synergy have emerged depending on whether active anions[10,14,21,24,25], cations[9,13,15,18,20], or organic species[19-20] are employed. However, a common theme throughout the literature is that one species adsorbs initially and bridges or facilitates the adsorption of the other species to produce a complex or layered barrier structure. These explanations continue to remain as theories. More germane to paints, synergistic combinations of paint additives have been explored since the late 1970's[26]. Examples include phosphates + borates, zinc phosphate + zinc nitrophthalate + zinc oxide, and more recently, zinc molybdate + zinc phosphate + a zinc salt of benzoic acid. This latter combination has been used in the DoD self-priming topcoat, which has unfortunately resulted in poor adhesion after limited service. This points out yet another hidden advantage of chromate pigments. In addition to having the appropriate balance of inhibitive power and solubility, an inhibitive pigment must not interfere with in-service adhesion, a property that is actually augmented by chromate pigments[27].

Recent studies have examined synergistic combinations of the previously described rare earth and transition metal salts[7,28,29]. Although these preliminary experiments have only examined 1:1 ratios of these materials at one concentration, synergistic effects have been observed using both electrochemical and pit morphology analyses. It is almost certain that the optimum ratio is something other than 1:1, and that a significant matrix of additional experiments is needed to identify the proper materials and ratio. Unfortunately, the predictive abilities and fundamental understanding of molecular systems with more than two or three different atomic species remains extremely limited, so that one is faced with a tortuous matrix of experiments to identify the optimum inhibitor combination under a wide range of test conditions (e.g. pH, T).

One approach to increase the rate of material discovery is through combinatorial approaches[30-32]. Combinatorics, initially utilized in electronic materials development[33], has been more commonly associated with automated synthesis and high throughput screening for pharmaceutical research. In the combinatorial process, large arrays of material or chemical variables can be produced and screened to identify the optimum process or condition of interest. Creation of the combinatorial libraries is typically straightforward. However, the identification of a rapid and dependable assay that can sensitively detect changes in the relevant parameter is not to be assumed and is often the rate limiting process in rapid discovery.

The corrosion protection properties of inhibitors can be electrochemically quantified in many different ways, however there no accepted electrochemical parameters that can be acquired rapidly (i.e. minutes) in the laboratory to predict long-term (i.e. years) corrosion protection. Yet, the desire is to screen thousands of chemical compounds with an infinite number of combinations in a vast number of environmental conditions (temperature, pH, concentration, etc.).

‡ USAF SAB, 1996

Chemical and electrochemical tests for high throughput screening of corrosion inhibitor performance have been identified for aluminum alloy AA2024. These methods have been shown to duplicate benchmark long-term (10 day) test data acquired using electrochemical impedance spectroscopy. Thus, a pathway has been created for the use of combinatorial approaches for rapid discovery of environmentally benign corrosion inhibitors as well identification of synergistic combinations.

The efficacious production of the central needs of this MURI requires dedicated instrumentation that will facilitate high throughput testing of corrosion inhibitors. More importantly, the educational mission to understand the structure-property relationships of inhibitor adsorption and function will require surface analysis instrumentation capable of analyzing the sequencing of events and orientation of compounds relative to the surface. This knowledge will help further focus the selection of effective inhibitor compounds.

II. Status of Program

The purchase of this equipment was delayed, however all equipment was ordered in late spring and has now been delivered. Item D arrived in September, hence the delay in report submission. The following equipment was purchased under this grant.

A. Multiple-Microelectrode Analyzer (Scribner Associates).

Through the use of conventional reaction frames fitted with the appropriate electrode configuration, it is anticipated that 96 experiments can be performed simultaneously. This will increase the throughput of electrochemical experimentation by a factor of ca. 100 at a minimum.

Estimated service life: greater than 10 years

B. Plate Reader (Molecular Devices)

Reaction frames used for the chemical detection of aluminum and other metal ion release can be read by an automated **plate reader**. This plate reader allows the sequential spectrometric analysis of a 96 well reaction frame in less time than has been used to analyze one sample up to now.

Estimated service life: greater than 10 years

C. Electrochemical Quartz Crystal Microbalance (CH Instruments)

Electrochemical experiments will provide a certain level of performance and mechanistic understanding. However, to significantly advance the educational process of understanding the mechanism of inhibitor performance, two additional pieces of equipment are requested. The surface adsorption characteristics of inhibitors as a function of the electrochemical status of the interface is essential to fully understand both the mechanism and boundaries of performance of a given inhibit compound. Adsorption characteristics of monolayers or less can be assessed very effectively with an **electrochemical quartz crystal microbalance** (EQCM). The EQCM will be very crucial to understanding the sequence of steps involved with the adsorption, bridging and performance of synergistic combinations of inhibitor species[35-36].

Estimated service life: greater than 10 years

D. Raman Spectrometer (Digilab)

Further insight into the mechanism of inhibitor adsorption and orientation of the inhibitor species to the substrate surface will be acquired via **Raman Spectroscopy** with surface enhancement. Raman Spectroscopy is a valuable tool for the characterization of materials due to its extreme sensitivity to the molecular environment of the species of interest, and is of particular importance to surface and near-surface species[37] such as corrosion inhibitors[38-42].

Molecular vibrations that produce Raman scattering must alter the polarizability of the molecule and complements the change in dipole moment detected by IR spectroscopy. This makes Raman Spectroscopy useful in the analysis of metal oxides.

An advantage of Raman spectroscopy is its accessibility to the low frequency of the spectrum (10-1 cm). This low frequency data is important in the complete vibrational analysis of surface species, especially for the investigation of the nature of chemical interaction of a surface species with the underlying surface. Again, this indicates that inhibitors can be investigated *in situ* without the concern for strong scattering as experience in IR spectroscopy.

In addition, the weak Raman scattering of water makes the Raman analysis of adsorbed species on electrode surfaces and polymers in aqueous media of particular importance. This will assist in the analysis of polymeric coating resins in another AFOSR funded project that seeks identify ionic channels in polymeric coating resins.

Estimated service life: greater than 10 years

III. Educational Benefit

The process of inhibitor discovery has historically occurred empirically. Due to the complexity of how inhibitors function, this process continues, although there is more insight now with the use of modern surface analysis methods such as Raman and EQCM. The educational mission of this research seeks to embrace the empirical process in its highest art, high throughput screening, to identify candidate compounds. More focused methods, Raman spectroscopy and EQCM, will then be used to elucidate the mechanism of inhibitor function. These methods will be even more essential for the understanding of synergy, a phenomenon that will likely be a requisite for future chromate replacements.

These methods will find extensive utility in other areas of research in these laboratories. For example, Raman spectroscopy will also aid in the investigation of coating resin degradation as a function of environmental exposure due to the weak Raman scattering by water. This will provide data in the investigation of environmental degradation mechanisms in organic coatings that is complementary to the typical electrochemical data acquired in these laboratories.

This equipment will provide invaluable skills and training for graduate students on topics relevant to the Department of Defense and civilian society. Research is presently under way.

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